FUNCTIONALIZATION AND CHARACTERIZATION OF MULTI-WALLED CARBON NANOTUBES/POLYPROPYLENE NANOCOMPOSITE

By

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ABSTRACT

Chemical and physical functionalization of multi-walled carbon nanotubes (MWCNT) have been commonly practiced to achieve better dispersion of carbon nanotubes in polymer matrix. However, not much is known about the effect of each functionalization method as well as a combination of both on the mechanical properties of carbon nanotubes/polypropylene nanocomposites. This work describes the various functionalization methods (acid-treatment, non-ionic surfactant treatment with Triton X-100), fabrication of MWCNT/PP nanocomposites via melt blending and injection molding as well as characterization of mechanical properties. Microscopy analysis (FESEM, TEM, XPS) showed effective purification of MWCNTs under acid treatment, and better dispersion under both chemical and physical functionalization techniques combined, in their respective order. Tensile tests showed increase in tensile strength for the nanocomposites that contain MWCNTs up to 2 wt%. A decrease in tensile strength was seen in samples that contain 4wt% of MWCNTs for both raw and Triton X-100 functionalized, signifying MWCNT degradation/rebundling at composition with higher content of MWCNTs. For the acid-treated MWCNTs, however, showed slight improvement even at 4wt%, showing a possibility of effective dispersion of MWCNTs.

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ABBREVIATIONS AND NOMENCLATURE

ASTM	American Society for Testing and Materials	**PA**	Polyamide
CMC	Critical Micelle Concentration	**PMMA**	Polymethylmethacrylate
CNT	Carbon Nanotube	**PN**	Polymer Nanocomposite
COOH	Carboxylic Acid	**PP**	Polypropylene
CVD	Chemical Vapor Disposition	**PP-g-MA**	Polypropylene-grafted-maleic anhydride
DMTA	Dynamic Mechanical Thermal Analysis	**PS**	Polystyrene
DSC	Differential Scanning Calorimetric	**PVA**	Polyvinyl Alchohol
EDX	Energy-dispersive X-ray spectroscopy	**SDBS**	Sodium Dodecyl Benzosulphonate
FESEM	Field Emission Scanning Electron Microscopy	**SDNT**	Small Diameter Nanotube
H_2SO_4	Sulphuric Acid	**SDS**	Sodium Dodecyl Sulphate
HNO_3	Nitric Acid	**SEM**	Scanning Electron Microscopy
iPP	Isotactic Polypropylene	**SWCNT**	Single-Walled Carbon Nanotube
MD	Molecular Dynamics	**TEM**	Transmission Electron Microscopy
MPTS	Methacryloxypropyltrimeth-oxysilane	**TGA**	Thermogravimetric analysis
MWCNT	Multi-Walled Carbon Nanotube	**THF**	Tetrahydrofurane
NH_2	Amine	**UTM**	Universal Testing Machine

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

The discovery of carbon nanotubes by Iijima [1] opened up a new era in materials science and nanotechnology. Because of their unique structural, electrical and mechanical properties carbon nanotubes (CNTs) have attracted much attention in the past several years. CNTs have high Young's modulus and tensile strength, and they can be metallic, semiconducting, or semimetallic, depending on the helicity and diameter. [2]

To-date, CNTs can be classified as single-wall (SWCNT), multiwall (MWCNT) and small-diameter (SDCNT) material. SWNTs are single-walled carbon nanotubes about 1nm in diameter with micrometer scale lengths; MWCNTs are multiwalled carbon nanotubes with an inner diameter of about 2 to 10nm, an outer diameter of 20 to 70nm, and a length of about 50μm; and SDCNTs have diameters of less than 3.5nm and have lengths from several hundred nanometers to several micrometers.

The introduction of inorganic nanoparticles as additives into polymer systems has resulted in polymer nanocomposites (PNs) exhibiting multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess. Among the improved properties of PNs are mechanical properties (increased modulus, stiffness, toughness), thermal expansion, thermal conductivity, ablation resistance, chemical resistance, dimensional stability, and reinforcement.

Polypropylene carbon nanotubes (CNT/PP) are a type of thermoplastic-based nanocomposite. The combination of lower densities and module of polymeric materials with thermally and/or electrically conducting CNT fillers allows the polymer formulator the opportunity to develop materials from insulating to conducting type characteristics.

1.2 PROBLEM STATEMENT

The arguments for the true mechanical properties of both single-walled and multi-walled nanotubes have never ceased. Some computational studies found that the true moduli of the nanotubes were far below the estimated values obtained from the graphene sheet. Molecular dynamics (MD) simulation is one of the useful tools to estimate the physical, mechanical and thermal properties of the nanotubes because it is able to reproduce the realistic nanotube structures. However, the time required for MD simulation is typically long and the investment on facilities is also huge.

Although so many efforts, focusing on different aspects of nanotubes and their co-related polymer-based composites have been paid to date, still no convergent results were obtained. This may be caused by the use of different approaches in theoretical and computational analyses. [3]

In this project, it is intended to discover the most effective uniform dispersion of CNT by suspending the CNTs (pristine and acid-treated for purification) in a nonionic solvent – Triton X-100. CNT/PP nanocomposites will be processed using the melt mixing method. The MWCNTs will be analyzed under Transmission Electron Microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), and Energy-Dispersive X-ray spectroscopy (EDX). Then, the mechanical properties of the nanocomposites are characterized by conducting mechanical tests using the Universal Testing Machine (UTM).

1.3 OBJECTIVES

The objectives of this project are:

1. To study the effects of acid treatment onto MWCNTs.
2. To investigate the effectiveness of MWCNTs functionalization with nonionic surfactant Triton X-100 in enhancing the mechanical properties of polypropylene nanocomposites produced under melt mixing.

1.4 SCOPE OF STUDY

The scope of study for this project include extensive research on two major areas:

- Multi-Walled Carbon Nanotubes (MWCNT)
- Polypropylene

The knowledge of the sub-topics required for the fields above include:

- Melt processing techniques to fabricate MWCNT/PP composites
- Chemical and physical functionalization methods to ensure uniform interfacial bonding between the carbon nanotubes and polypropylene
- Transmission Electron Microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM) and Universal Testing Machine (UTM) techniques to characterize the mechanical properties of MWCNT/PP nanocomposites.

CHAPTER 2

LITERATURE REVIEW

In 1991, the discovery of carbon nanotubes by Iijima[1] has created a revolution in the world of nanomaterials engineering. Due to its wide range of potential uses, research after research has been done to create various polymer carbon nanocomposites. Carbon nanotubes exist in two main forms: Single-walled (SWCNT) and Multi-walled (MWCNT). Unlike SWCNTs, MWCNTs are easier to manufacture using the popular technique of chemical vapour deposition (CVD) and is lower in cost.

Polypropylene composites have a vast range of applications. From aerospace and automobile applications to the packing industry [23], PP/CNT nanocomposites have garnered much interest among scientists to fabricate PP/CNT nanocomposites in different techniques as well as functionalization of MWCNTs to provide effective dispersion in their polymer composites [4].

Shaffer and Windle [5] conducted the first study of using nanotubes as reinforcement of solution-based composites in 1999. DMTA (Dynamic Mechanical Thermal Analysis) measurements on CVD-MWCNT-PVA films with nanotube weight fractions up to 60% were carried out. Very little reinforcement was observed, as the storage modulus increased from approximately 6 GPa for the polymer to 12 GPa for the 60 wt% composite film. They managed to conclude that it is easier to reinforce softer matrices, as better results were obtained above the polymer glass transition temperature. Using short fiber theory, the nanotube modulus and effective length obtained were 150 MPa and 35 nm, respectively. The low modulus value may be due to the difficulty in fitting a highly non-linear function such as Krenchel's rule

of mixtures to a limited data set. As a first attempt, it was proven the reinforcement was possible, albeit leaving much room for improvement and further research.

2.1 Melt Processing and Characterization of Mechanical Properties

Melt processing is a common alternative for preparing polymer nanotube composites, and is particularly effective for thermoplastic materials such as polypropylene. This technique takes advantage of the fact that thermoplastic polymers soften when heated. Amorphous polymers can be processed above their glass transition temperature while semi-crystalline polymers need to be heated above their melt temperature to induce sufficient softening. [6, 7] The advantages of this technique are its speed and simplicity, and its compatibility with standard industrial techniques.

Melt processing involves the melting of polymer pellets to form a viscous liquid. Any additives, in this case, such as CNTs can be mixed into the melt by shear mixing. Bulk samples can then be fabricated by techniques such as compression molding, injection molding or extrusion. However it is important that processing conditions are optimised not just for different nanotube types, but for the whole range of polymer-nanotube combinations. This is because nanotubes can affect melt properties such as viscosity, resulting in unexpected polymer degradation under conditions of high shear rates. [8]

In 2001, Jin et al. [9] carried out analysis of mechanical properties of bulk composites fabricated by melt-processing. They mixed polymethylmethacrylate (PMMA) with MWCNT in a laboratory mixing moulder. TEM studies showed that dispersion was good even at high MWNT concentration. By testing PMMA doped with Arc-MWCNT by DMA they discovered an increase in Young's modulus from 0.7 GPa to 1.63 GPa at 17 wt% nanotubes. The results showing a level of reinforcement of approximately 7 GPa coincided with Shaffer and Windle's [5] first study.

Not long after, in year 2002, Andrew and co-workers [10] showed that commercial polymers could be melt processed with CVD-MWCNT to form composites. The polymers were blended with nanotubes at high loading level in a high shear mixer to form masterbatches that were then mixed with pure polymer to form lower mass fraction samples. Films were formed by compression molding. The results achieved showed an increase in modulus from ~2 GPa to ~2.6 GPa and ~4.5 GPa at 5 wt% and 25 vol.% respectively, providing reinforcement levels of 9 and 19 GPa. Also, in both studies [9, 10] craze formation was observed in microscopy studies with nanotube pullout observed at the fracture surface.

Shear mixing can sometimes be difficult because nanotube powder tends to stick to the walls of the mixer. A combination of solution and melt techniques can be used to overcome this problem. Thostenson and Chou [11] dispersed CVD-MWCNT in a solution of PS in tetrahydrofurane (THF). This was then drop cast and dried to form a film. The film was cut up and extruded through a rectangular die. Films could be formed by compression molding or alternatively the nanotubes could be aligned by drawing the sample direct from the extruder. Thostenson and Chou [11] discovered that the nanotubes that were pulled out from the matrix was still coated with polymer, showing the presence of very strong interfacial bonding, resulting in good adhesion and wetting.

Zhang et al. [12] successfully prepared MWCNTs/nylon-6 (PA6) nanocomposites in 2003 by simple melt-compounding and showed significant improvement in mechanical properties compared with neat PA6. Upon incorporation of only 1 wt% MWCNTs, the elastic modulus of PA5 is improved by about 115% from 396.0 to 852.4 MPa, and the tensile strength at yield is improved by about 124% from 18.0 to 40.3 MPa. The composite became somewhat brittle compared with neat PA6 (which breaks above 150% of elongation) as the elongation break of the composite was about 125%. Overall the tensile test results showed that

the mechanical properties of MWCNTs/PA6 composite are superior to those of neat PA6, due to reasons such as:

i) The reinforcement of finely dispersed high-performance MWCNTs nanofillers throughout the polymeric matrix

ii) Strong interaction between MWCNTs and nylon-6 matrix

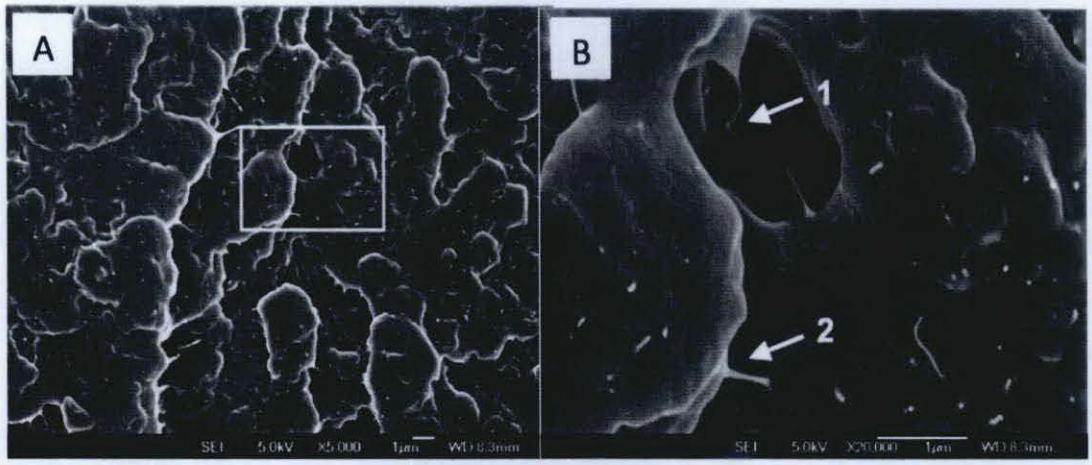

Fig 1. (A) SEM image showing an overall morphology of failure surface for PA6 nanocomposite containing 1 wt% MWCNTs. (B) Enlarged morphology of selected region in (A). Reproduced from [11].

It was in year 2004, however, that various significant improvements in research were reported. Meincke et al. [13] fabricated composites from CVD-MWCNT in polyamide-6. They used injection molding to fabricate the composites in a twin screw extruder at 260°C. TEM showed good nanotube dispersions.

The modulus increased from 2.6 to 4.2 GPa at 12.5 wt% corresponding to a reinforcement value of ~34GPa. A significant reduction in ductility was also detected, from 40% to 4%. Blend composites were also made from polyamide-6, ABS and nanotubes. The results showed modest increase from 1.97 to 2.51 GPa at 7.5 wt%. The reinforcement value stood at 11 GPa. This phenomenon can be partly explained by the fact that the nanotubes were observed by TEM to reside only in the PA-6 phase. In the three phase blends the ductility fell from 105% to 40%, and the impact strength decrease by a factor of 2.

Also in 2004, Zhang et al. [12, 14] made composites from CVD-MWCNT in polyamide-6. An increase in modulus was detected from 0.4 GPa to 1.24 GPa in addition of 2 wt% nanotubes.

The reinforcement value was at an impressive ~64 GPa. There was also a significant increase in yield strength from 18 to 47 MPa and similar increases was observed in ultimate tensile strength. In addition, there was no decrease in toughness and the ductility fell slightly from 150% to 110%. These encouraging results were due to good dispersion and adhesions observed by microscopy measurements.

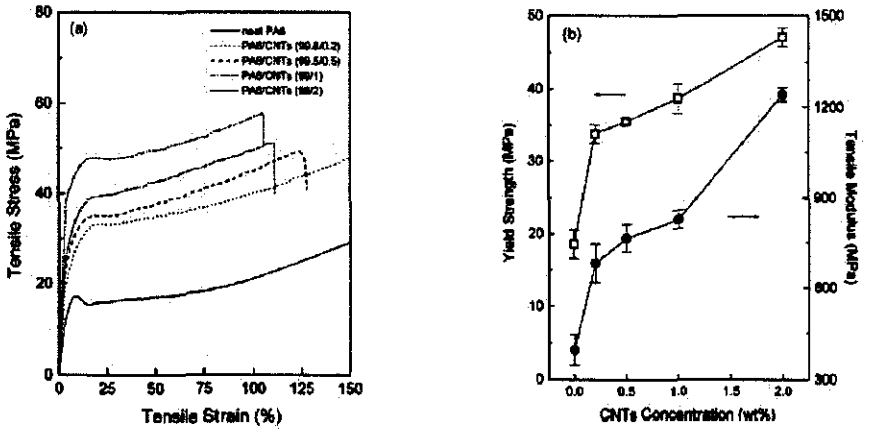

Fig 2. (a) Stress-strain curves and (b) yield strength and modulus for PA6-MWCNT composites. Reproduced from [12].

A study was done on aligning carbon nanotubes in polypropylene matrix by melt spinning using two different weight percentages (0.5 and 1.0 wt%) of nanotubes for the synthesis of the nanocomposite fibers. [15] For the fiber synthesis, a ThermoHaake™ Minilab co-rotating twin-screw extruder was used. The operating temperature was elected after conducting differential scanning calorimetric (DSC) scan and thermogravimetric analysis (TGA) on the pure polymer. The screw speed was set on 60 rpm and the polymer and MWCNT were allowed to mix for 60 minutes. The composite fiber was extruded from a die of 0.5 mm diameter and spun onto a take up spool using a fiber-spinning apparatus. The take up speed was maintained constant to obtain a uniform diameter fiber. For drawing the fiber a known load (2.5g) was attached to one end of the fiber and allowed to hang in a furnace, which was maintained at 90°C.

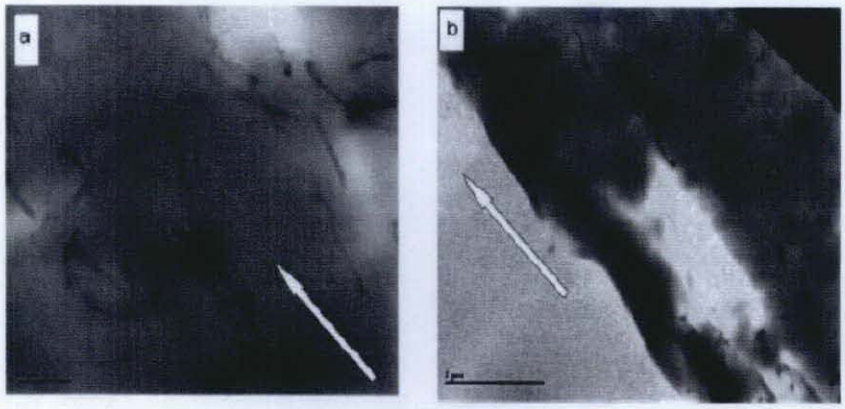

Fig 3. Longitudinal TEM images of PP/0.1 wt% MWCNT sample. The arrows denote orientation of MWNTs along the fiber axis. Reproduced from [15].

For nanotube loading of 0.5 wt% the tensile properties showed more than a threefold increase in the tensile modulus and strength when compared with pure PP fibers (1.0 GPa to 3.1 GPa, and 25 MPa to 80 MPa, respectively). With a nanotube loading of 1.0 wt% the modulus increased 3.7 times (1.0 GPa to 3.7 GPa) and strength increased 5 times (25 MPa to 125 MPa) compared with pure PP. Consistent with previous attempts and studies, this also showed that the significant property enhancement was due to highly dispersed and well aligned CNTs, and/or good adhesion between the nanotubes and the polymer matrix. This results in good load transfer from the polymer matrix to the nanotubes. Further increase in the strength was observed when the fibers were drawn, suggesting further alignment of the nanotubes.

Sometime in 2007, Zhao et. al [16] fabricated a series of composite consisted of iPP/PP-g-MA/MWCNTs (90/10/x wt%; x = 0, 0.1, 0.3) by melt-mixing. The specimens are termed as PPCNTx (where x represent the weight content of the PPCNT multiplied by 10, such as PPCNT3 means that the MWCNTs content is 0.3 wt%) and PPCNT0 is regarded as matrix resin (iPP/PP-g-MA 90/10 wt%).

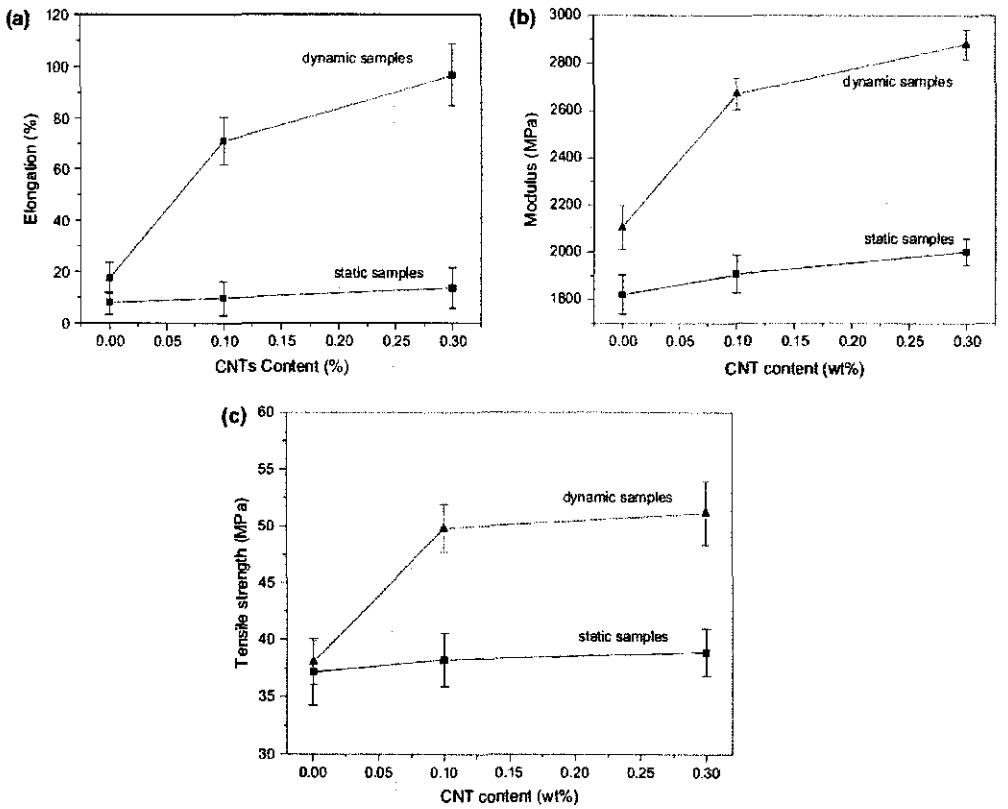

Fig 4. CNT content dependences of: (a) elongation, (b) Young's modulus, (c) tensile strength in the as-prepared composites. Reproduced from [16].

By adding 0.1 wt% and 0.3 wt% of MWCNTs, the increase in the ductility was found to be about 800% to 1000%, respectively, as compared with the static sample of iPP/PP-g-MA matrix; at about 400% and 540% respectively, compared with the dynamic sample of iPP/PP-g-MA matrix. The Young's modulus of iPP/PP-g-MA matrix via DPIM is 2.1 GPa and increased to 2.6 GPa and 2.8 GPa by adding 0.1 wt% and 0.3 wt% MWNTs, respectively; and the tensile strength correspondingly increased from 38.0 MPa to 49.8 MPa and 51.1 MPa.

Bikiaris et al. [17] studied the effects of acid treatment multi-walled carbon nanotubes on the mechanical stability of isotactic polypropylene (iPP). Their purpose was to modify the MWCNTs by introducing surface carboxylic groups through treatment, due to the nanotubes' length reduction and formation of surface reactive groups, on the filler's dispersion and nanocomposites' mechanical properties.

The MWCNT nanocomposites were prepared by melt-mixing, and four different nanotubes were used: untreated MWCNTs and acid treated (nitric acid and sulfuric acid) and refluxed for different times (15, 30, 60 minutes). The samples were washed and then dried under vacuum at 100°C. As a result, the length of the MWNTs progressively decreased as the treatment time was increased.

The mechanical properties of the nanocomposite was tabulated as in Table 1:

Table 1. Mechanical Properties of PP nanocomposites containing 2.5wt% MWCNTs before and after acid treatment. Reproduced from [17]

Sample	Stress at yield (MPa)	Stress at break (MPa)	Elongation at break (MPa)	Young's Modulus (MPa)
iPP	27.9 ± 0.4	28.7 ± 0.6	640 ± 30	600 ± 60
iPP/2.5wt% MWNT	-	31.0 ± 1.2	4.9 ± 0.3	1330 ± 30
iPP/2.5wt% MWNT15	-	32.7 ± 1.3	5.2 ± 0.2	1370 ± 40
iPP/2.5wt% MWNT30	-	34.5 ± 0.9	6.6 ± 0.2	1420 ± 70
iPP/2.5wt% MWNT60	-	27.0 ± 1.5	4.7 ± 0.6	1220 ± 90

Bao and Tjong [18] prepared PP nanocomposites reinforced with 0.1, 0.3, 0.5 and 1.0 wt% MWCNTs using melt-compounding in a twin-screw extruder followed by injection molding. Bao and Tjong altered the loading rate and temperature parameters of the twin-screw extruder to investigate their impacts on the mechanical properties.

The mechanical properties of PP and PP/MWCNT nanocomposites obtained at a moderate cross-head speed of 10 mm min^{-1} under 18°C were charted in the table below. As proven before, it was observed that the additions of very small amounts of MWCNTs to PP improve its yield strength and Young's modulus considerably. The stiffness of PP increased dramatically by ~31% by adding 0.3 to 0.5 wt% MWCNTs. The storage modulus also detected an increase from 1.88 to 2.5 GPa, about 33% improvement over pure PP.

In compliance with the loading rate and temperature parameters altered, Bao and Tjong concluded that PP/MWCNTs nanocomposites tend to increase with increasing test temperatures, indicating that the reinforcing effect of MWCNTs in PP matrix is more pronounced at higher temperatures.

Table 2. Mechanical Properties of PP and MWCNT/PP nanocomposites. Reproduced from [18]

Specimens	Yield Strength (MPa)	Young's modulus (MPa)	Storage Modulus (GPa)
Pure PP	30.71 ± 0.18	1570 ± 24	1.88
PP/0.1 wt% MWCNT	34.89 ± 0.39	1743 ± 65	2.40
PP/0.3 wt% MWCNT	35.98 ± 0.27	2107 ± 72	2.50
PP/0.5 wt% MWCNT	35.88 ± 0.39	2070 ± 66	2.51
PP/1.0 wt% MWCNT	35.65 ± 0.41	2056 ± 83	2.49

Hou and co-workers investigated the structural orientation and tensile properties on the extrusion-elongated sheets of CNT/PP composites in 2008.[19] Two means were used to achieve a well dispersion of MWCNTs within the PP matrix, as that: (1) modification of raw MWCNTs through grafting C18 alkyl chains on the backbones of nanotubes; (2) incorporation of 10wt% maleic acid anhydride-grafted PP (PP-g-MA) acted as compatibilizer. In order to estimate the effect of structural orientation on the tensile properties, the orientation level of composite sheets was adjusted through applying various drawn speeds after extrusion. The MWCNTs were modified with reactive grafting with octadecylamine to enhance the capability of dispersion in PP matrix. The tensile behavior of the extrusion-drawn sheet was significantly impacted by both adding MWCNTs and increase of drawn speed.

About the same time, Zhou et al. [20] functionalized MWCNTs with a silane coupling agent. Methods of functionalization of MWCNTs with silane coupling agents often cause the structure destruction of MWCNTs. Zhou and co-workers first coated the MWCNTs with inorganic silica by a sol-gel process and then grafted with 3-methacryloxypropyltrimethoxysilane (3-MPTS) to prevent destruction of the MWCNTs fine graphite sheets structure. The TEM images showed that a uniform

layer of silane has been formed on the surface of MWCNTs after functionalization with 3-MPTS.

It was observed that the tensile strength of PP composites increases with the increasing MWCNTs content. When MWCNT content reached 1 wt%, the tensile strength of the CNT/PP composite was highest. With even more addition of MWCNTs, agglomerates of MWCNTs form in the PP matrix due to the difficulty of homogenous dispersion of MWCNTs via melt mixing, which led to the decrease of tensile strength. However, at the same content, the PP/3-MPTS functionalized MWNCTs composites had higher tensile strength than PP/raw MWCNT composites.

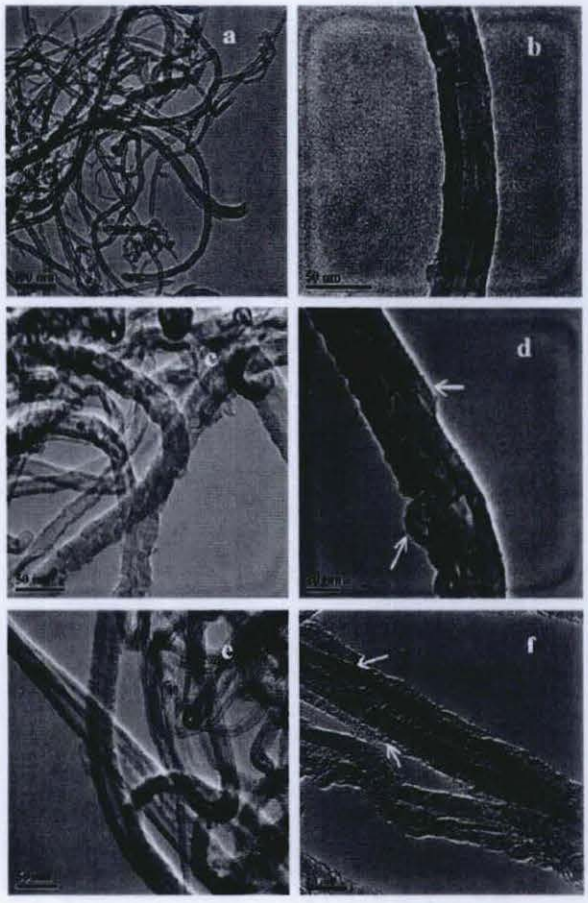

Fig 5. TEM images of (a & b) the raw MWNTs; (c & d) silica-coated MWNTs; (e & f) 3-MPTS functionalized MWNTs.

Yang and co-workers[21] grafted PP onto MWCNTs by melt-blending PP containing 0.6 wt% of maleic anhydride and amine-functionalized MWCNTs and then evaluated the mechanical properties of the PP/PP-g-MWCNTs. Pristine MWCNTs were first treated with a 3:1 mixture of concentrated sulfuric and nitric acid. The mixture was then sonicated at 40oC for 3 hours in an ultrasonic bath,

followed by dilution in cold distilled water. The acidified MWCNTs (MWNT-COOH) were separated and washed repeatedly with distilled watter. MWNT-COOH was then allowed to react with ethylenediamine to afford MWCNT-NH_2.

PP-MA and MWCNT-NH_2 were blended to ensure a complete conversion of amine groups of MWCNT-NH_2 to imide groups. The melt blending was accompanied by the formation of bubbles due to the release of water vapor during the reaction process. The blending stopped after the formation of bubble stopped.

The dispersion of PP-g-MWCNTs in the composites were shown in TEM and SEM micrographs. While the grafting of PP onto MWCNTs helped disperse the nanotubes in the matrix, it remains a challenge to completely disperse PP-g-MWCNTs in the PP matrix at higher PP-g-MWCNTs contents.

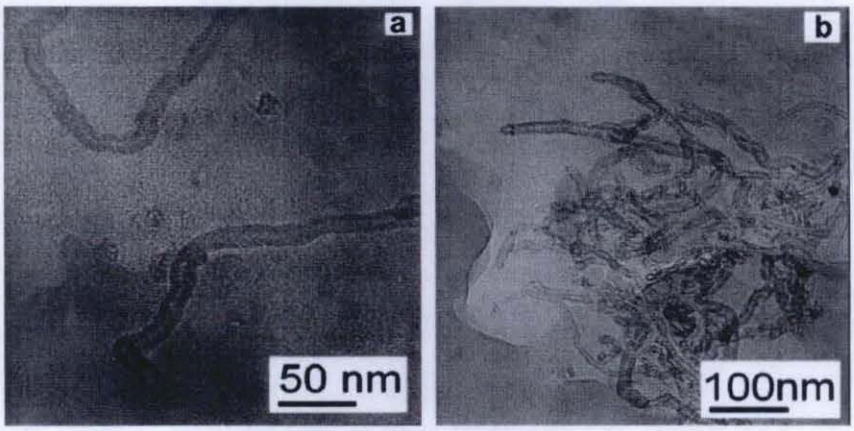

Fig 6. TEM micrographs: (a) PP/PP-g-MWCNTs composite, (b) PP/MWCNTs composite. The effective MWCNT contents of both composites are 1.0 wt%. Reproduced from [21]

When PP was reinforced was pure MWCNTs, its Young's modulus and tensile strength increased, but its ultimate strain and toughness were reduced. On the other hand, the Young's modulus, tensile strength, ultimate strain and toughness of PP were improved with the addition of PP-g-MWCNTs with an effective MWCNTs content of 1.5 wt%. It was deduced that PP-g-MWCNTs are more effective than organoclay in enhancing mechanical properties of PP.

Table 3. Tensile properties of PP and composites. Reproduced from [21]

MWNTs content	Tensile Strength / (MPa)	Ultimate Strain / (mm/mm)	Toughness (MJ/m^3)	Young's Modulus (MPa)
0%	25.16 ± 0.15	0.072 ± 0.005	1.29 ± 0.18	773 ± 12
0.5%PG	39.14 ± 0.29 (+56%)	0.076 ± 0.007 (+6%)	2.03 ± 0.15 (+57%)	1123 ± 15 (+45%)
1.0%PG	53.15 ± 0.36 (+111%)	0.098 ± 0.006 (+36%)	3.77 ± 0.20 (+192%)	1324 ± 19 (+71%)
1.5%PG	60.74 ± 0.38 (+141%)	0.107 ± 0.008 (+49%)	4.99 ± 0.23 (+287%)	1610 ± 23 (+108%)
2.0%PG	54.64 ± 0.42 (+117%)	0.077 ± 0.005 (+7%)	3.11 ± 0.27 (+141%)	1684 ± 25 (+118%)
1.0%AR	31.11 ± 0.38 (+24%)	0.042 ± 0.005 (-42%)	0.82 ± 0.12 (-36%)	1032 ± 17 (+34%)

PG = PP-g-MWNTs; AR = pristine MWNTs. Value in parentheses represents percentage change as compared to PP.

Lee et al. [22] attempted to disperse nitric acid treated MWCNTs in polypropylene using maleic anhydride grafted polypropylene (MA-g-PP) and butanol/xylene solvent mixture. Evidence for hydrogen bonding between maleic anhydride grafted polypropylene and nitric acid treated MWCNTs was obtained using infrared spectroscopy. Tensile tests show that there was an increase in tensile strength and Young's modulus, while dynamic mechanical tests show that the storage modulus increased by a larger scale at a higher temperature, suggesting temperature dependant interfacial strength, similar to Bao and Tjong's [18] findings.

In the same year, Yang et al.[23] also performed mechanical tests onto PP/PP-g-MWCNT composites. The Young's modulus, tensile strength, ultimate strain and toughness of PP were improved by 108, 141, 49 and 287% respectively, by the addition of PP-g-MWCNTs with an effective MWCNTs content of 1.5 wt%. They concluded that PP-g-MWCNTs are more effective than organoclay in enhancing the mechanical properties of PP.

In 2009, Thiebaud [24] investigated the mechanical properties of PP/MWCNT composites in four different grades: 1 wt%, 2 wt%, 4 wt% and 8 wt%. The composites were fabricated using the melt-mixing method. It is observed that there was an increase of the Young's modulus and the stress at fracture with the MWCNT level while the strain to failure decreases significantly. The results obtained is as shown in Figure 7 and Table 4:

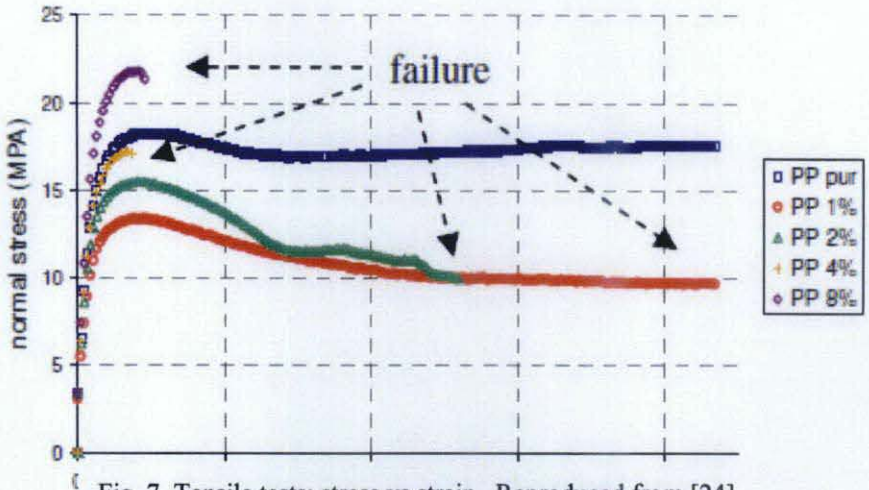

Fig 7. Tensile tests: stress vs strain. Reproduced from [24]

Table 4. Young's Modulus and Rupture Strain. Reproduced from [24]

MWCNT level (wt%)	Young's Modulus (MPa)	Stress at Fracture (MPa)
1	484	Ø
2	604	10
4	694	17
8	849	21

2.2 Current Advancement in Dispersion of Carbon Nanotubes

As carbon nanotubes are being used vastly as matrix reinforcement, more and more studies are being done to uncover more effective methods of dispersing carbon nanotubes to maximize its great potential.

In 2008, Lie et al. performed the ultracentrifuge method to characterize carbon nanotube dispersions. [28] The MWCNTs were first ultrasonicated in dfferent surfactants (SDBS - sodium dodecylbenzene-sulfonate, Triton X-100) in varying time duration in an ice bath. To determine the sedimentation function of the given SWCNTs, the diluted samples were subjected to ultracentrifugation for different periods of time. The supernatant was then extracted and subjected to absorption spectrum measurements with a UV-vis-NIR spectrometer as shown in Figure 8.

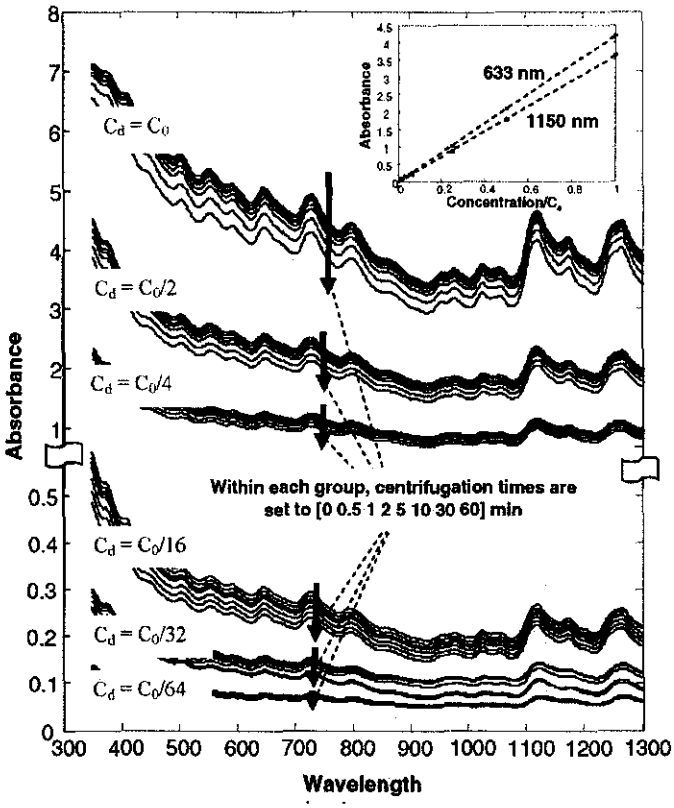

Figure 8. UV-vis-NIR spectra for the 12 h sonicated SWCNT/SDBS/ H2O dispersions. The group of Cd) C0 represents the as-prepared and corresponding supernatants centrifuged for various times. Others represent the series-diluted dispersions and corresponding centrifuged supernatants. The inset plot shows the absorbance vs concentration of the series dispersions without centrifugation.

Reproduced from [28].

A burst of progress in the research of dispersing carbon nanotubes took place most aggressively in year 2010. Rausch and co-workers investigated the dispersibility of unfunctionalized and three differently functionalized multi-walled carbon nanotubes in the presence of anionic, cationic and non-ionic surfactants. [29]

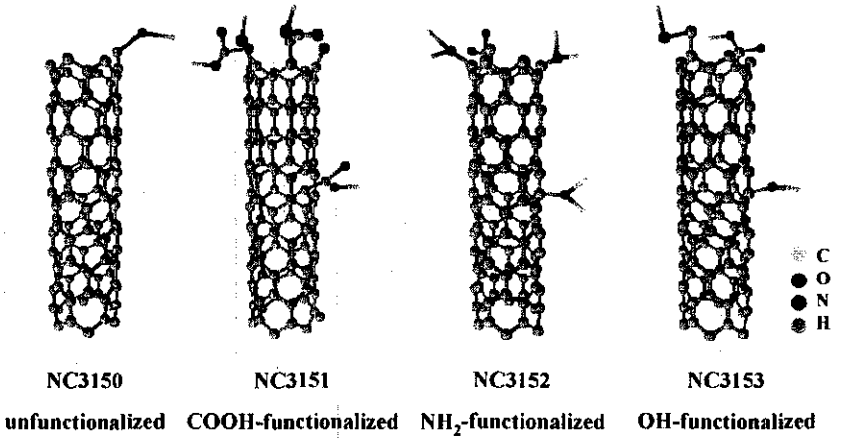

Figure 9. Schematic representation of the differently functionalized MWCNTs. Reproduced from [29]

The mixtures were sonicated and cooled in water bath in different time intervals and recorded with UV-vis-spectrometer. It was found that at short sonication times the absorbance increases rapidly before leveling off at intermediate at higher sonication times. It was recommended that proper adjustment of the surfactant to CNT weight ration is necessary for optimal exfoliation of the CNT.

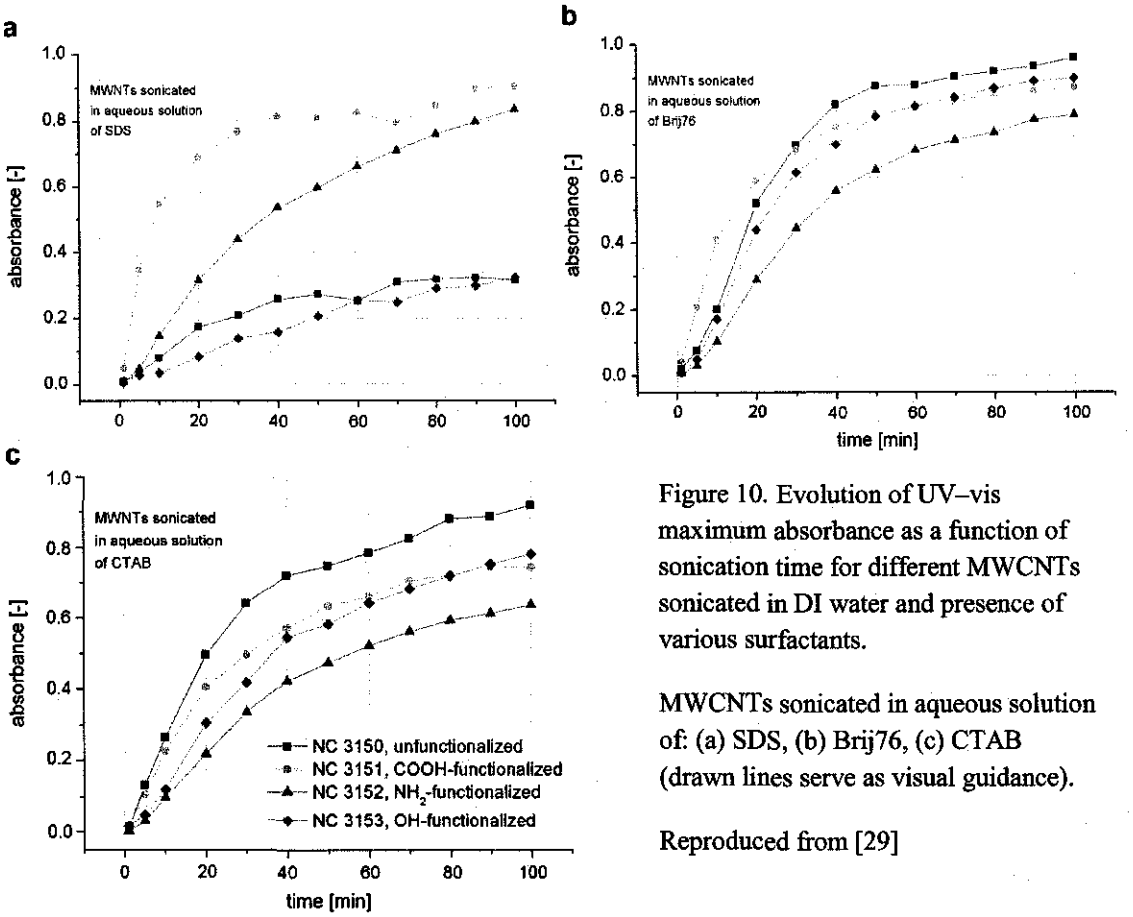

Figure 10. Evolution of UV–vis maximum absorbance as a function of sonication time for different MWCNTs sonicated in DI water and presence of various surfactants.

MWCNTs sonicated in aqueous solution of: (a) SDS, (b) Brij76, (c) CTAB (drawn lines serve as visual guidance).

Reproduced from [29]

Bai and co-workers selected the Triton-X series surfactants with a same hydrophopic functional group and different hydrophilic polyethoxyl chain lengths to investigate their adsorption onto CNTs and their ability to stabilize CNT suspensions. The samples were shaken in a Gyrotory shaker at 200 rpm for 48 hours, and then underwent entrifugation at 3000g for 30 minutes. The samples were tehn filtered to remove the suspended CNTs but not significantly remove the surfactants. They discovered that adsorption capacities of the surfactants increased with decreasing hydrophilic chain length: Triton X-305 < Triton X-165 < Triton X-114 < Triton X-100. It was also found out that suspended CNT amounts in water were

positively related to the adsorption capacities of the surfactants, but negatively with the hydrophilic fraction ratio of the X-series surfactants. [30]

Comparative studies on dispersing multi-wall carbon nanotubes using two anionic surfactants (sodium dodecyl sulphate, SDS and sodium dodecyl benzosulfonate, SDBS) were also conducted. [31]. CNTs were shorted by boiling in concentrated HNO_3 for 1 hour, and added to the surfactant solutions of different concentrations that are close to the critical micelle concentration (CMC) of both SDS and SDBS and sonicated for 5 hours at room temperature. The CNTs dispersions were then centrifuged to remove the precipitates and non-dispersed material. It was found that both dispersing agents form stable suspensions even below their CMC limit.

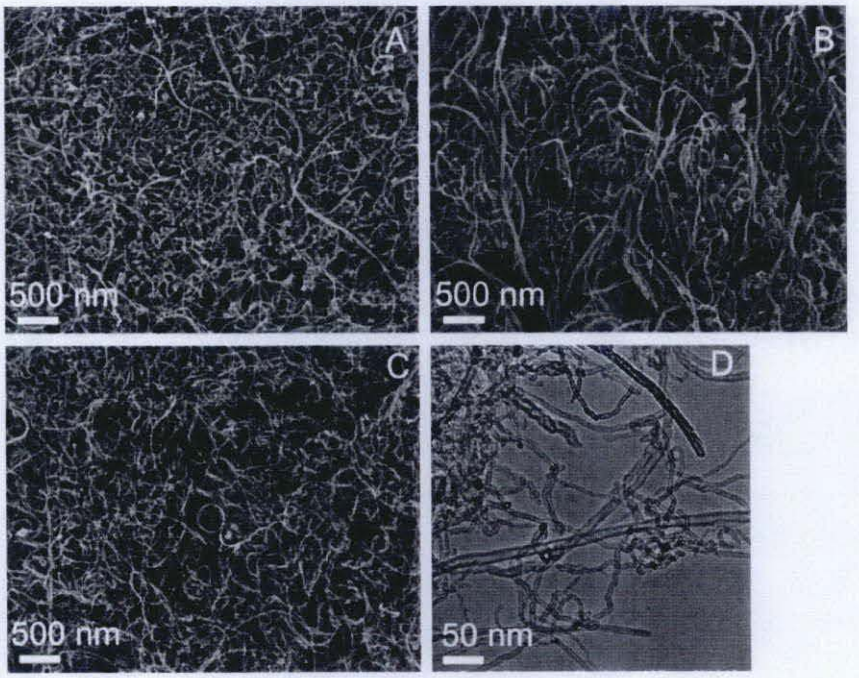

Figure 11. SEM and TEM images: pristine CNTs (A), non-dispersed CNTs (B), CNTs recovered from dispersion (C and D). Reproduced from [31].

CHAPTER 3

METHODOLOGY

3.1 Fabrication of CNT/PP Composites

Melt processing comprises of melting polymer pellets to form a viscous liquid, with carbon nanotubes as an additive to be mixed into the melt through shear mixing. The samples are then fabricated by techniques such as injection molding. Optimum processing conditions have to be determined (type of solvent, injection molding operating conditions such as pressure, temperature, etc.) to ensure uniform interfacial bonding between the nanotubes and polypropylene. [2]

In melt-mixing, there are several ways of obtaining a better dispersion of MWCNTs during the preparation of the composite. It is worthwhile to explore the possibilities of increasing the potential of the MWCNTs by performing chemical and physical functionalization before fabrication of the nanocomposite. Based on the literature reviews that have been studied, the procedures of preparation of MWCNT/PP nanocomposites has been designed into three parts:

3.1.1 Part 1: Purification of MWCNT with acid solution

The MWCNTs used in this experiment is purchased from Senzhen Nanotech Port Co. Limited and are of 40nm to 60nm diameter in size. An acid solution of H_2SO_4 and HNO_3 is mixed in a 3:1 ratio. To test the effect of ultrasonication time to the dispersion and purification of MWCNTs, a few parameters is set to make a substantial comparison.

The parameters are fixed as shown:

Table 5. Parameters of Acid Treatment of raw MWCNTs

Ratio of acid solution to MWCNT	Ultrasonication Time
150 ml acid, 1 g raw MWCNT	0.5 hours
150 ml acid, 1 g raw MWCNT	2.75 hours
150 ml acid, 1 g raw MWCNT	5 hours

Samples are then filtered with with a microfiltration system, using a cellulose membrane filter of 0.47 μm pore size. Then the filtered MWCNTs are left to dry for 12 hours at room temperature, and then in a vacuum oven of 100°C for 5 hours. Samples are taken for FESEM and XPS analysis and the best sample is identified to be used for making of the nanocomposite.

3.1.2 Part 2: Functionalization of raw and purified MWCNTs

Both raw and purified MWCNTs from Part 1 are then suspended in the Triton X-100 solution (5mg/ml), and sent for ultrasonication for 1 hour. The ratio of MWCNTs to surfactant is 1g MWCNT: 1.5g Triton X-100. The carbon nanotubes are filtered, washed and dried to be used for fabrication of the nanocomposite.

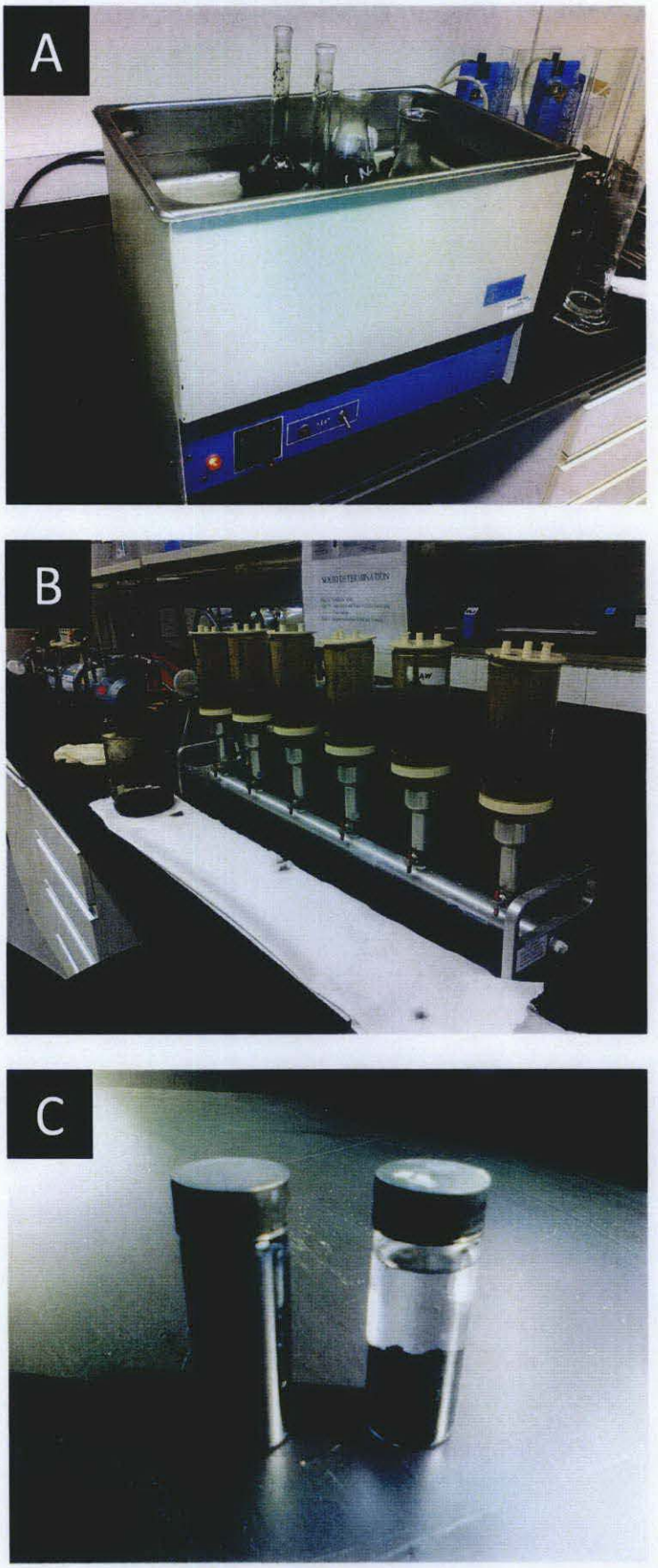

Figure 12. Images from purification and functionalization processes; (A) ultrasonication, (B) microfiltration, (C) suspended MWCNTs in Triton-X after (left) and before (right) ultrasonication.

3.1.3 Part 3: Fabrication of PP/MWCNT Nanocomposite

Once the parameters in Part 1 and Part 2 are determined and chosen, bulk samples of functionalized MWNTs as much as 12 grams are produced for fabrication of the nanocomposite. Polypropylene and the MWCNTs are mixed using the Haake Rheomix 600 mixer under temperatures of 200°C, mixing speed of 30 rpm and a mixing duration of 15 minutes. The polypropylene was allowed to be melted for 5 minutes prior to adding the MWCNTs, in 0.5, 1.0, 2.0 and 4.0 wt%.

Subsequently, the mix is granulated into pellets and sent to Petronas Research Sdn Bhd in Bangi, Selangor to be directly injection molded with the Krauss Maffei 40 Tonne injection molding machine into dog bone samples, adhering to the standard of ASTM D638. The injection molding parameters are as follows; barrel temperature: 205 – 220°C, mould temperature: 25°C, pressure: 800 bar, speed: 60 rpm.

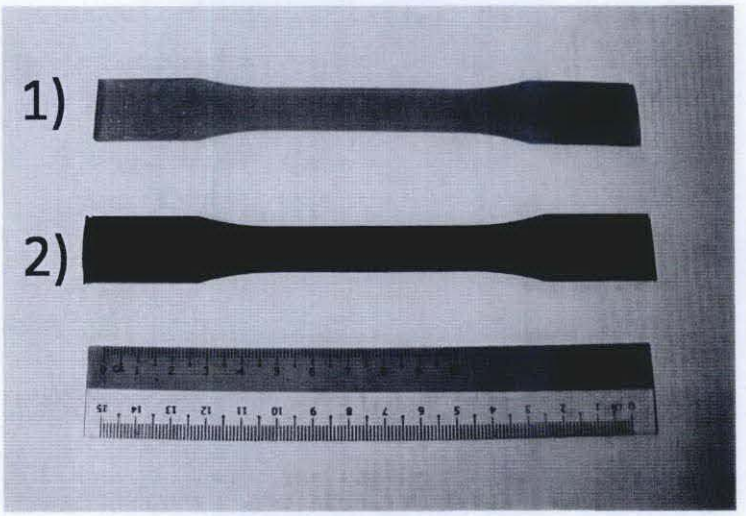

Figure 13. Dogbone specimens according to ASTM D638 standards;
(1) Pure PP, (2) MWCNT/PP nanocomposite

3.2 Characterization and Mechanical Testing of Composites

a. Transmission electron microscopy (TEM) and Field Emission Scanning Electron Microscopy (FESEM)

TEM, EDX and FESEM are used to check the MWCNT configuration after purification under acid treatment. Unlike the light microscope, the TEM and FESEM use electrons instead of light. The electrons function as "light source" and their much lower wavelength makes it possible to get a resolution of a few angstroms (10^{-10} m). As a result, these electron microscopes are able to provide small area crystallographic information of the nanocomposite. EDX is used to determine the composition of materials/elements in the MWCNTs. The FESEM, EDX and TEM analysis are done in the university's Central Research Laboratory.

b. Mechanical tests with the Universal Testing Machine (UTM)

The UTM is used to conduct tensile tests onto the fabricated MWCNT/PP composite. Results of these tests show the characterization of the mechanical properties of the composite materials in forms of shear-strain graphs.

3.3 Milestones (for Gantt Chart, refer to Appendix A)

Table 6. Milestone for Final Year Project I

No.	Item	Due (Week)	Status
1.	Selection of Project Topic	2	Completed
2.	Preliminary Research Work Completion of Literature Review	5	Completed
3.	Submission of Preliminary Report	5	Completed
4.	In-depth Study of Related Topic Obtaining Quotation from Vendors	7	Completed
5.	Submission of Progress Report	8	Completed
6.	Seminar	8	Completed
7.	Identify related parameters	11	Completed
8.	Material Procurement	11	Completed
9.	Fabrication of First CNT/PP Sample	13	Completed
10.	Submission of Interim Report Final Draft	14	Completed
11.	Oral Presentation	14	Completed

Table 7. Milestone for Final Year Project II

No.	Item	Due (Week)	Status
1.	Confirming parameters and bulk processing of functionalized MWCNT	9	Completed
2.	Submission of Progress Report	8	Completed
3.	Fabrication of CNT/PP Samples TEM, SEM and Mechanical Testing	10	Completed
4.	Submission of Progress Report 2	8	Completed
5.	Pre-SEDEX	11	Completed
6.	Submission of Draft Report	11	Completed
7.	Submission of Dissertation, Technical Paper	12	Completed
8.	Oral Presentation	13	
9.	Submission of Dissertation (hard bound)	7 Days after Oral Present.	

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results and Analysis

4.1.1 Purification of MWNT with acid treatment

The samples were sent for FESEM and EDX inspection, with a clear disctinction of purification and shortening of MWCNTs in different ultrasonication time. The FESEM results are shown in Figure 14. Not much difference can be seen on the structure of MWCNTs after 0.5 hours of ultrasonication, but more obvious changes are found from the samples that have undergone ultrasonication for 2.75 hours and 5 hours. At 5 hours, the MWCNTs are severely shortened and dispersed, with the risk of the MWCNTs being damaged under prolonged acid treatment.

The EDX results in Figure 15 show that the Fe catalyst were eliminated and Ni was reduced significantly after acid treatment. However, oxidation also occurred more aggressively under longer periods of ultrasonication. Based on our reference[29], the optimum parameter obtained is the ultrasonication time of 2.75 hours, in 150 ml of acid solution, whereby a sufficient amount of Ni was reduced without a drastic oxidation of carbon. The presence of sulphur is due to the acid treatment, and can be removed with thorough washing. TEM micrographs (Fig. 16) confirm the effectiveness of purification of the MWCNTs.

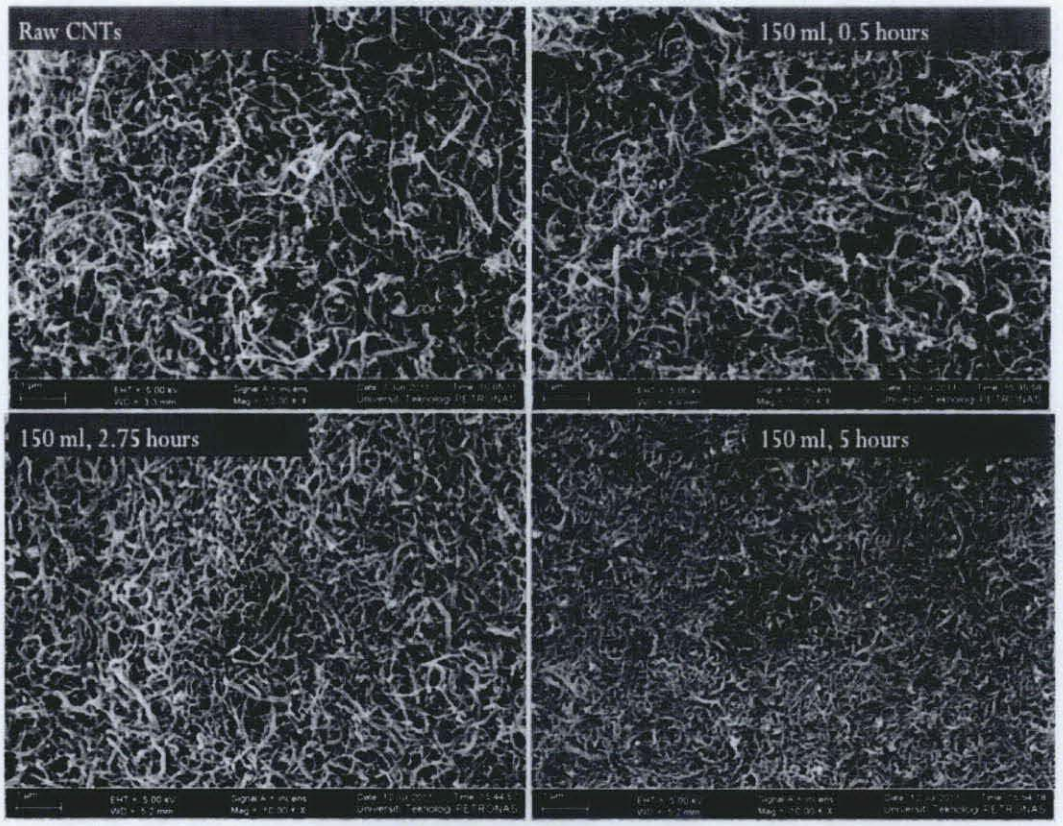

Figure 14. FESEM images (10K times of magnification) of MWCNTs after acid treatment under different ultrasonication hours; Clockwise from top-left: Raw CNTs, 0.5 hours, 2.75 hours, 5 hours.

Raw CNTs

Element	Weight%	Atomic%
C K	94.22	96.52
O K	4.04	3.11
Fe K	0.46	0.10
Ni K	1.29	0.27
Totals	100.00	

150 ml 2.75 hours

Element	Weight%	Atomic%
C K	90.56	93.40
O K	7.95	6.16
S K	0.73	0.28
Ni K	0.76	0.16
Totals	100.00	

150 ml 5 hours

Element	Weight%	Atomic%
C K	88.93	91.82
O K	10.26	7.95
S K	0.32	0.12
Ni K	0.50	0.10
Totals	100.00	

Figure 15. EDX results after acid treatment under different ultrasonication hours

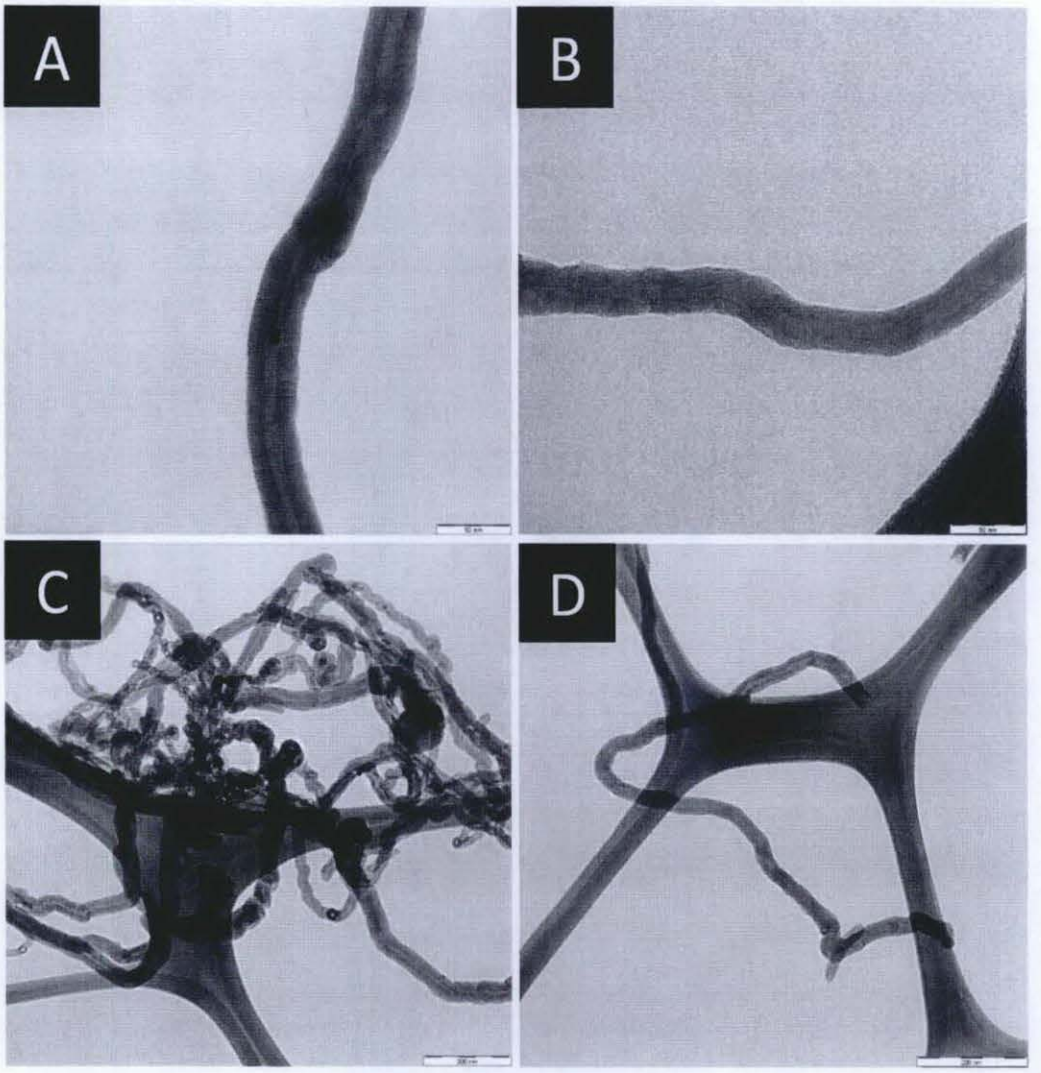

Figure 16. TEM micrographs showing impurities contained in raw MWCNTs (A and C), and purified MWCNTs after 2.75 hours of acid treatment (B and D).

4.1.2 MWCNTs Functionalization with Triton X-100 and the Mechanical Properties of PP/CNT nanocomposite

While anionic, cationic and nonionic surfactants have been used in previous studies to disperse carbon nanotubes, a nonionic surfactant was chosen for this experiment due to polypropylene's insolubility in water. Triton X-100 was used due to its availability in the market and previous studies have shown that it was an effective dispersing agent. [30]

Melt-mixing was chosen over solution mixing due to time constraints and the first being a preferred choice for bulk production. It was also intended to combine the shear force of melt mixing with the functionalized MWCNTs to achieve better dispersion of MWCNTs. However, it was found that the functionalized MWCNTs form a hardened deposit after filtration and drying. A mortar grinder was used to grind the deposit into powder-form again before adding into the melt-mixer.

Tensile tests with the rate of 20mm/min was performed onto the dogbone specimens adhering to ASTM D638 standards, and stress-strain graphs [Figure 17 to 19] were obtained. The resulting tensile strength and Young's modulus are obtained as in Table [8].

Table 8. Tensile test results for PP/CNT nanocomposite samples

Sample	Tensile Strength (MPa)	Percentage Increase (%)	Percentage Strain at Maximum (%)	Young's Modulus (Mpa)
PP	28.96	-	-	-
PP + 0.5wt% raw MWCNT	30.31	4.64	16.95	496.00
PP + 1.0wt% raw MWCNT	32.47	12.11	16.43	528.03
PP + 2.0wt% raw MWNT	33.32	15.04	16.89	558.42
PP + 4.0wt% raw MWNT	32.56	12.42	12.49	553.12
PP + 0.5wt% TX MWCNT	31.62	9.18	17.78	499.90
PP + 1.0wt% TX MWCNT	32.12	10.88	17.43	524.91
PP + 2.0wt% TX MWCNT	33.69	16.32	16.78	545.10
PP + 4.0wt% TX MWCNT	33.36	15.16	13.04	557.16
PP + 0.5wt% A-TX MWCNT	30.83	6.45	17.31	487.04
PP + 1.0wt% A-TX MWCNT	32.90	13.59	16.73	536.35
PP + 2.0wt% A-TX MWCNT	33.63	16.09	16.47	533.26
PP + 4.0wt% A-TX MWCNT	**33.98**	**17.32**	**16.04**	**566.38**

R: Raw MWNT; TX: Triton X-100 functionalized MWNT; ATX: Acid-treated and Triton X-100 functionalized MWN

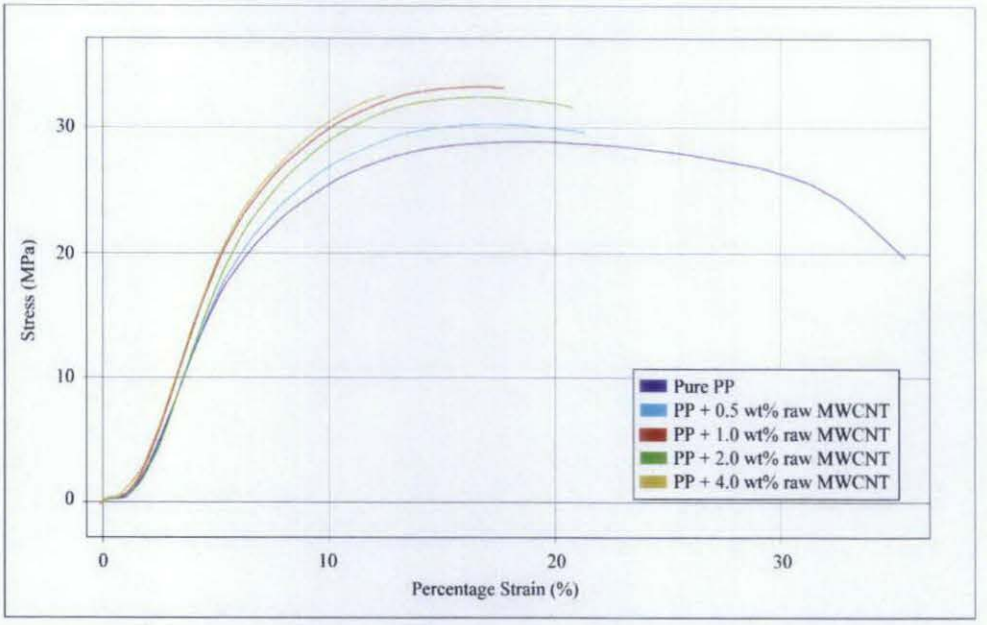

Figure 17. Stress-strain diagram for raw MWCNT/PP nanocomposite

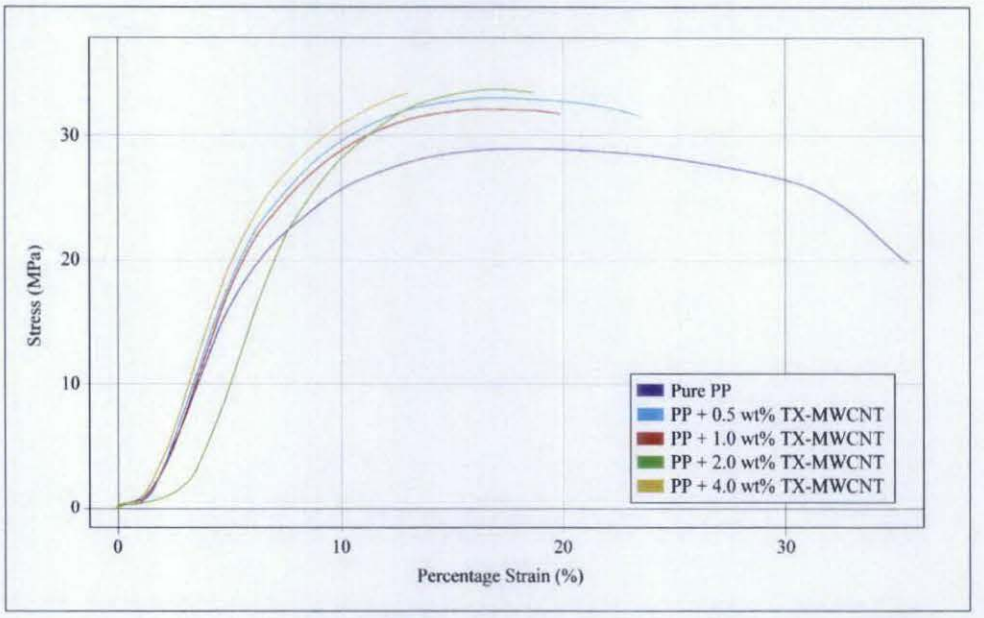

Figure 18. Stress-strain diagram for Triton X-100 functionalized MWCNT/PP nanocomposite

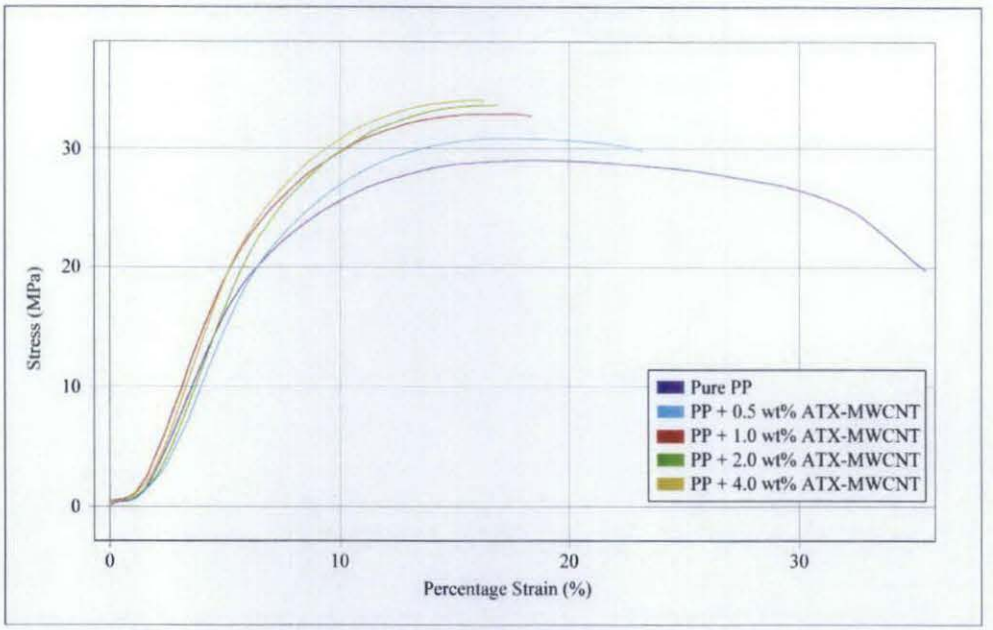

Figure 19. Stress-strain diagram for acid-treated and Triton X-100 functionalized MWCNT/PP nanocomposite

From the results obtained from the tensile test, it is observed that the PP nanocomposites exhibit higher mechanical performance with increasing MWCNT content up to 2 wt% for all samples. For samples containing raw and functionalized MWCNTs without acid treatment experience a slight decrease in tensile strength at 4%. This confirms studies that show that partial tensile strain can be transferred to MWCNTs embedded in PP matrix under tensile stress in low MWCNTs content. However, further addition of MWCNTs causes agglomerates of MWCNTs to form in the PP matrix and defects appear in the polymer matrix due to poor MWCNT dispersion by melt mixing. [32] Samples with MWCNTs that underwent acid treatment on the other hand showed encouraging results with continuous increase of tensile strength even at 4wt% of MWCNTs content. This shows that purified and shortened MWCNTs continue to achieve good dispersion within the polymer matrix.

4.2 Problems Encountered

a) Low quality MWCNTs

When the raw MWCNTs were scanned under FESEM, it was seen that the diameter of the MWCNTs were inconsistent and did not adhere to the specifications as provided by the supplier. Also, EDX results (Fig 15) showed a high amount of catalyst in the MWCNTs.

b) Slow filtration and waste of MWCNTs

Due to the small diameters, MWCNTs were easily trapped in the pores of the membrane filters, causing the filtration process to be largely time-consuming, and the filters had to be changed frequently to speed up the process. MWCNTs deposits are lodged firmly in the filters, and a small amount is wasted each time the filter is changed.

c) Hardened deposit of filtered and dried MWCNTs

The MWCNTs that were filtered and dried formed a hardened deposit, which could cause uneven dispersion in mixing with the PP matrix during melt-mixing. While the hardened deposit was successfully grinded into powder-form, the grinding also resulted in damage to the MWCNTs by causing more open ends.

d) Contamination of MWCNTs

MWCNTs were exposed to foreign materials during two stages of the experiment, due to improper cleaning of equipment. The two stages were:

- **Mortar grinding.** Foreign materials from previous usages are deeply embedded in the walls of the grinding container, hence it was almost impossible to remove the contaminants with normal cleaning. The contaminants came in contact with MWCNTs during the grinding process.

- **Granulator.** Due to safety reasons, certain areas of the granulator could not be cleaned or vacuumed, causing the pellets to be in contact with foreign materials from the previous use. Even though the pellets were thoroughly cleaned with water subsequently, some foreign fibers remained, and could be seen compromising the tensile test when the contaminants were seen at the fracture surface of the dogbone specimens.

e) Inability to optimize the functionalization of MWCNTs with nonionic surfactant, Triton X-100

Functionalized MWCNTs were filtered, washed and dried before the melt-mixing process. This causes the surfactant to be removed, making the functionalization process almost redundant. Physical functionalization can only be effective when suspended or coated in the surfactant that is compatible with the matrix. Therefore, this project has been unsuccessful in dispersing MWCNTs using Triton X-100 under melt-mixing process. An alternative approach is suggested for future experiments.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Based on the results obtained, it can be seen that acid treatment effectively removes and reduces catalysts in MWCNTs, as well as shortening the tubes. However, prolonged treatment can also damage the MWCNTs, forming amorphous carbon around the walls as well as reducing its mechanical properties. Throughout the experiments, it was concluded that 2.75 hours was the optimum ultrasonication time to purify the MWCNTs.

Also, it has been proven that purification and shortening of MWCNTs contribute to more effective dispersion of MWCNTs in the polymer matrix. The shortening of MWCNTs enables the MWCNTs to be dispersed more effectively in the PP matrix by delaying agglomeration to higher loadings.

The objectives of this project have been achieved rather successfully, although certain recommendations have been listed in the next section.

5.2 Recommendations

Based on the problems faced throughout the project, there are a few recommendations to be taken into account should another experiment be designed to achieve similar objectives:

a) Purchase higher quality MWCNTs

Higher quality MWNTs contain less catalysts and more consistent diameter sizes. MWNTs with low catalyst content require less intense acid treatment and will be able to preserve more amount of carbon from being oxidized, thus optimizing the mechanical properties.

b) Use new/clean equipment

To preserve the purity of MWCNTs, it is recommended to use new equipment that have not been in contact with other materials. It is very crucial to ensure that MWCNTs are not contaminated to maximize its mechanical properties and to prevent complications during the production of the nanocomposites.

c) Using the Solution Mixing approach

For experimental purposes, the solution mixing approach is more suitable as MWCNTs can be suspended in a compatible surfactant with the polymer matrix, thus enabling the surfactant to effectively disperse the MWCNTs. Also, this approach will prevent the hardening of the MWCNTs deposits as the MWCNTs will be suspended in a solution. A custom-made mold that adheres to ASTM D638 standards will have to be used to produce the suitable dogbone specimens for tensile testing.

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APPENDICES

APPENDIX A – GANTT CHART

Table 8. Gantt Chart for Final Year Project I

No.	Detail / Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
1.	Selection of Project Topic	■	■													
2.	Preliminary Research Work Completion of Literature Review		■	■	■	■										
3.	Submission of Preliminary Report					√										
4.	In-depth Study of Related Topic Obtaining Quotation from Vendors					■	■		■							
5.	Submission of Progress Report									√						
6.	Seminar									√						
7.	Identify and obtain related parameters					■	■		■	■	■	■	■			
8.	Material Procurement											■	■			
9.	Fabrication of First CNT/PP Sample												■	■	■	
10.	Submission of Interim Report Final Draft															√
11.	Oral Presentation															√

Mid Semester Break

Table 9. Gantt Chart for Final Year Project II

No.	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1.	Fabrication of CNT/PP Samples TEM, SEM and Mechanical Testing	■	■	■	■	■	■	■								
2.	Submission of Progress Report									√						
3.	Fabrication of CNT/PP Samples TEM, SEM and Mechanical Testing									■	■	■	■			
4.	Pre-EDX												√			
5.	Submission of Draft Report													√		
6.	Submission of Dissertation (Soft Bound)														√	
7.	Submission of Technical Paper														√	
8.	Oral Presentation									During Study Week						
9.	Submission of Dissertation (hard bound)									7 Days after Oral Presentation						

Mid Semester Break

APPENDIX B – MWNT CERTIFICATE OF ANALYSIS

深圳市纳米港有限公司
ShenzhenNanotechPortCo.,Ltd.

CERTIFICATE OF ANALYSIS

Product	L-MWNT-4060		
Items	Test methods	Nominal	Results
Appearance		Black Powders	Black Powders
Diameter	**TEM**	40-60nm	40-60nm
CNTs content (%)	**TEM, TPO**	>95	>95
Length	**TEM**	5-15μm	5-15μm
SSA	**BET**	40-300m2/g	40-300m2/g
Ash	**EDS, TGA**	<2%	